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Heat-shrinking Polyester Film

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SPECIFICATION

1. Title of the Invention

Heat-shrinking polyester film

2. Claims

(1) Thermoplastic {It should be heat-shrinking. -- Translator} polyester film, prepared from a polyester composition which contains 100 weight units of a polyester, consisting of a dicarboxylic acid component and a diol component, and 1 - 40 weight units of at least one plasticizer selected from phthalate ester plasticizers, polyester plasticizers, aliphatic dicarboxylate ester plasticizers, aliphatic mono-carboxylate ester plasticizers, phosphate ester plasticizers, citrate ester plasticizers, epoxy plasticizers, trimellitate ester plasticizers, tetrahydrophthalate ester plasticizers, glycol plasticizers, and bisphenol A-alkylene oxide derivatives {It should be adducts. -- Translator}.

3. Detailed Explanation of the Invention

Industrial field of utilization

This invention concerns a heat-shrinking polyester film. In more detail, this invention concerns a heat-shrinking polyester film which has excellent low-temperature shrinking property as well as a uniform shrinking capability and is very suitable as a shrink label material for various kinds of containers.

Prior art

Heat-shrinking films are capable of shrinking upon reheating and have been widely used for various purposes, such as shrink package, shrink label, cap seal, etc.

Shrink labels for various kinds of containers, including poly(ethylene terephthalate) (PET) containers, glass containers, etc., are mainly made from monoaxially stretched films of poly(vinyl chloride), foamed polystyrene, etc. Of these films, heat-shrinking poly(vinyl chloride) film is most commonly used because of its good low-temperature shrinking capability and printing properties.

However, poly(vinyl chloride) has a relatively low heat resistance and will generate hydrogen chloride when incinerated. Moreover, when heat-shrinking poly(vinyl chloride) film is used as a heat-shrinking label, it can not be recovered and recycled together with the PET container.

On the other hand, heat-shrinking polyester film, such as poly(ethylene terephthalate) film, etc., has an excellent heat resistance and will not generate hydrogen chloride when incinerated. These are properties that the poly(vinyl chloride) film does not have. Therefore, it is highly desirable to use heat-shrinking polyester film as material for heat-shrinking labels to replace the heat-shrinking poly(vinyl chloride) film.

However, since a polyester polymer usually has high crystallinity, the heat-shrinking polyester film has a relatively high heat-shrinking temperature. In addition, the shrinking ratio will show a sudden increase as the temperature increases, which will cause problems in processability and shrinking homogeneity when used for heat-shrinking labels for containers.

Recently, several improvements have been proposed for heat-shrinking polyester films.

For example, Japanese patent Kokai Sho 57-42726 reported a heat-shrinking film which is transparent, has good heat-sealing property, and can be used as a packing film material. The film is prepared from a copolyester consisting of terephthalic acid as the dicarboxylic acid component and ethylene glycol and 1,4-cyclohexanedimethanol as the diol component.

Japanese patent Kokoku Sho 63-7573 showed that the high crystallinity can be reduced and consequently the shrinking property as well as the heat-sealing property can be improved by having isophthalic acid as a copolymer component.

Moreover, in Japanese patent Kokoku Sho 64-10332, a highly shrinkable polyester film was reported, which can be prepared from a polyester composition

containing a noncrystalline copolyester, consisting of terephthalic acid or its derivatives and ethylene glycol and 1,4-cyclohexanedimethanol, and a polyester, consisting of terephthalic acid or its derivatives and ethylene glycol.

In the above patents, as the raw material for heat-shrinking polyester film, noncrystalline copolyester or a mixture of noncrystalline copolyester with crystalline polyester is used to reduce the crystallinity of polyesters. As compared to the heat-shrinking film prepared from crystalline poly(ethylene terephthalate), the film obtained by the above method has a large shrinking ratio, high heat-sealing strength, low shrinking stress, improved shrinking homogeneity, and less cracking problem on the heat-sealing part.

However, the present state-of-the-art technology still cannot provide a heat-shrinking polyester film with sufficient shrinking.

In other words, as compared to the heat-shrinking poly(vinyl chloride) film, the heat-shrinking polyester film obtained by the above method still has the shortcomings of high shrinking temperature and sudden increase of the shrinking ratio at a temperature when shrinking starts.

Because of these shortcomings, the processability in the shrinking process will be low and the shrinking homogeneity is not very good. Especially, when it is used as a shrink label for a container, because of the difference between the cap part and the body part, the sudden increase of the shrinking ratio as the temperature increases may result in uneven sealing as well as in distortion of the letter printing. It is not good in practical use.

<u>Problems to be solved by the invention</u>

The purpose of this invention is to provide a heat-shrinking polyester film which has excellent low-temperature shrinking property as well as uniform shrinking capability.

In order to overcome the shortcomings of the current technology mentioned above, the inventors carried out a series of studies. As a result, it was found that a heat-shrinking polyester film prepared from a polyester composition, which contains a polyester, consisting of a dicarboxylic acid component and a diol component, and a plasticizer selected from phthalate ester plasticizers, polyester plasticizers, aliphatic dicarboxylate ester plasticizers, aliphatic monocarboxylate ester plasticizers, phosphate ester plasticizers, citrate ester plasticizers, epoxy plasticizers, trimellitate ester plasticizers, tetrahydrophthalate ester plasticizers, glycol plasticizers, bisphenol A-alkylene oxide derivatives {adducts?}, etc., can have a shrinking temperature as low as that of the heat-shrinking poly(vinyl chloride) film, a gradual increase of the shrinking ratio with increasing the temperature, and a uniform shrinking capability.

This invention has been completed based on the above discovery.

Techniques used in solving the problems

This invention provides a heat-shrinking polyester film prepared from a polyester composition which contains 100 weight units of a polyester, consisting of a dicarboxylic acid component and a diol component, and 1 - 40 weight units of at least one plasticizer selected from phthalate ester plasticizers, polyester plasticizers, aliphatic dicarboxylate ester plasticizers, aliphatic monocarboxylate ester plasticizers, phosphate ester plasticizers, citrate ester plasticizers, epoxy plasticizers, trimellitate ester plasticizers, tetrahydrophthalate ester plasticizers, glycol plasticizers, and bisphenol A-alkylene oxide derivatives {adducts}.

In the following, this invention is explained in detail.

Polyester

The polyesters used in this invention can be derived from a dicarboxylic acid component and a diol component, from a hydroxycarboxylic acid component, or from a mixture of these components. The dicarboxylic acid component includes, for example, terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, di-phenylenedicarboxylic acid, diphenyl ether dicarboxylic acid, phenylenediacetic acid, adipic acid, azelaic acid, sebacic acid, oxalic acid, succinic acid, malonic acid, glutaric acid, pimelic acid, suberic acid, dodecanedioic acid, cyclohexanedicarboxylic

acid, carbonic acid, etc. The diol component includes, for example, ethylene glycol, propylene glycol, neopentyl glycol, butanediol, hexanediol, 1,4-cyclohexane-dimethanol, diethylene glycol, polyalkylene glycol, xylylene glycol, hydroquinone, resorcinol, dihydroxydiphenyl, bisphenol A-alkylene oxide adduct, etc. The hydroxy-carboxylic acid component includes, for example, hydroxybenzoic acid, hydroxyalkyl-benzoic acid, hydroxyalkoxylphenylacetic acid, hydroxynaphthoic acid, glycolic acid, etc.

Of these polymers, the polyester containing 50 mole % or more of terephthalic acid as the dicarboxylic acid component and 50 mole% or more of ethylene glycol as the diol component is very suitable for this purpose, because of the low crystallinity and good heat-sealing properties.

The plasticizer used in this invention should be at least one plasticizer selected from the plasticizers described above. More detailed examples are as follows.

The phthalate ester plasticizers include, for example, dialkyl phthalates, such as dibutyl phthalate, dioctyl phthalate, diheptyl phthalate, etc., dibenzyl phthalate, etc.

The polyester plasticizers include, for example, a polymer of ethylene glycol, propylene glycol, 1,3-butanediol, 1,6-hexanediol, etc., with adipic acid, sebacic acid, phthalic acid, etc.

The aliphatic dicarboxylate ester plasticizers include, for example, dioctyl adipate, diisodecyl adipate, dioctyl azelate, dihexyl azelate, dioctyl sebacate, di-isooctyl sebacate, etc.

The aliphatic monocarboxylate ester plasticizers include, for example, butyl stearate, amyl stearate, butyl oleate, etc.

The phosphate ester plasticizers include, for example, trioctyl phosphate, triphenyl phosphate, diphenyl 2-ethylhexyl phosphate, etc.

The citrate ester plasticizers include, for example, tributyl citrate, tributyl acetylcitrate, tri(2-ethylhexyl) acetylcitrate, etc.

The epoxy plasticizers include, for example, epoxidized soybean oil, epoxidized linseed oil, octyl epoxy stearate, etc.

The trimellitate ester plasticizers include, for example, tributyl trimellitate, trihexyl trimellitate, trioctyl trimellitate, etc.

The tetrahydrophthalate ester plasticizers include, for example, dioctyl tetrahydrophthalate, diisodecyl tetrahydrophthalate, etc.

The glycol plasticizers include, for example, poly(ethylene glycol), poly(ethylene glycol) benzoate, etc.

Moreover, the bisphenol A-alkylene oxide derivatives (adducts?) can be, for example, a compound obtained by an addition reaction of ethylene oxide or propylene oxide with bisphenol A.

These plasticizers can be used alone or as a mixture containing two or more of them.

Mixing Ratio

In this invention, the mixing ratio of the polyester and plasticizer described above should be in the range of 1 - 40 weight units of the plasticizer, preferably 2 - 30 weight units, to 100 weight units of the polyester. The best mixing ratio is in the range of 3 - 15 weight units of the plasticizer to 100 weight units of the polyester.

By mixing with the plasticizer described above, the crystallinity of the polyester can be reduced. In addition, when the polyester is used in a heat-shrinking film, the shrinking can start gradually at a relatively low temperature since the polymer molecular chains can slide more easily along each other. If the amount of the plasticizer added is less than 1 weight unit, the polymer molecular chains will

have less sliding capability and, at a relatively low temperature, the shrinking property will be insufficient. On the other hand, if the amount of the plasticizer added is more than 40 weight units, the modulus of elasticity of the film at the stretching temperature used in the film preparation will decrease significantly. The stretching will become very difficult and a heat-shrinking film cannot be obtained.

Furthermore, any common additives, such as fillers, coloring agents, etc., can be added to the composition of this invention if necessary.

Preparation of the heat-shrinking film

The plasticizer-containing polyester composition can be melt-extruded into a sheet with common methods, such as T-die method, tubular method, etc., to give an unstretched film. The unstretched film thus obtained is then stretched about 1.5 - 6 times at least in one direction by a roller, tenter, tubular method, etc., to give a desired heat-shrinking polyester film.

Mechanism

Because of the effect of the plasticizer, the plasticizer-containing heat-shrinking polyester film obtained above starts to shrink at a relatively low temperature around 70°C, which is almost the same as that of the heat-shrinking poly(vinyl chloride) film.

Moreover, the heat-shrinking ratio increases gradually, as the temperature increases from the shrinking temperature.

Therefore, the heat-shrinking polyester film obtained above can be used as a shrink label for containers which have a small body part, such as bottles, etc., and a big cap part. Since the shrinking ratio increases gradually, the shrink label made from the heat-shrinking polyester film can give a uniform shrinking as well as excellent sealing which can cover both the small part and big part without generating any distortions of the printing.

The heat-shrinking polyester film has a higher heat resistance than the heat-shrinking poly(vinyl chloride) film. For example, it can be used as the shrink label for PET containers and retorting treatment will not affect the label.

Furthermore, the heat-shrinking polyester film will not generate hydrogen chloride when incinerated as the heat-shrinking poly(vinyl chloride) film does. Besides, the heat-shrinking polyester film is basically made from the same material as PET containers, so that by using the polyester film of this invention as the shrink label, PET containers can be recovered with the label on.

As described above, as compared to the conventional heat-shrinking polyester film, the heat-shrinking polyester film of this invention has a relatively low temperature shrinking capability and improved processability. In addition, since the heat-shrinking ratio increases gradually as the temperature increases, uniform shrinking can be obtained without generating any distortions.

Practical Example

In the following, this invention is explained with practical examples and comparative examples.

Moreover, in the following, 'unit' means weight unit.

Practical Example 1

A polymer composition containing 100 units of a copolyester, consisting of terephthalic acid as the dicarboxylic acid component, 70 mole % of ethylene glycol and 30 mole % of 1,4-cyclohexanedimethanol as the diol component, and 5 units of dibutyl phthalate (DBP) as the plasticizer, was melt-extruded to give an unstretched film with a thickness of 120 μm.

The unstretched film obtained above was stretched threefold at 80°C in the transverse direction to give a heat-shrinking film with a thickness of 40 μm.

The shrinking ratios in transverse direction of the heat-shrinking film obtained above were measured at each 10°C increase in a temperature range of 60°C - 110°C.

The film was cut in the transverse direction to give a sample sheet with a length of 100 mm and width of 10 mm, which was placed in a hot air flow at the measuring temperature for 5-minute shrinking, and then the shrinking ratio of the sample was measured.

Practical Examples 2 - 19

Except for using the composition containing 100 units of the polyesters and 5 units of the plasticizers listed in Table 1, the heat-shrinking films were prepared with the same procedure as in Practical Example 1 and then evaluated with the same method as in Practical Example 1.

Comparative Examples 1 - 2

Except that the polyesters listed in Table 1 were used in the absence of any plasticizers, the heat-shrinking films were prepared with the same procedure as in Practical Example 1 and then evaluated with the same method as in Practical Example 1.

The results obtained from Practical Example 1 - Practical Example 19 and Comparative Examples 1 - 2 are shown in Table 2.

Table 1 (part 1)

Practical example	Polyester		Plasticizer
	dicarboxylic acid	diol	
	[the numbers in ( ) are in mole %]		
1	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol(30)	dioctyl phthalate (DOP)
2	terephthalic acid (90) isophthalic acid (10)	ethylene glycol	dioctyl phthalate (DOP)
3	poly(ethylene terephthalate)		diheptyl phthalate (DHP)
4	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol(30)	poly(phthalate ester) (Polysaisa-P-29 (?) *1)
5	terephthalic acid (90) isophthalic acid (10)	ethylene glycol	poly(adipate ester) (Polysaisa-W-4000(?) *2)
6	poly(ethylene terephthalate)		poly(sebacate ester) (Polysaisa-P-202(?) *3)
7	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol(30)	dioctyl sebacate (DOS)
8	terephthalic acid (90) isophthalic acid (10)	ethylene glycol	dioctyl azelate (DOZ)
9	poly(ethylene terephthalate)		dioctyl adipate (DOA)

Note) *1, *2, and *3 are available from Dainippon Ink Kagaku Kogyo Co., Ltd.

Table 1 (part 2)

Practical example	Polyester		Plasticizer
	dicarboxylic acid	diol	
	[the numbers in ( ) are in mole %]		
10	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol (30)	butyl oleate (BO)
11	terephthalic acid (90) isophthalic acid (10)	ethylene glycol	butyl stearate (BS)
12	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol (30)	diphenyl 2-ethylhexyl phos-phate (DEP)
13	terephthalic acid (90) isophthalic acid (10)	ethylene glycol	trioctyl phosphate (TOP)
14	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol (30)	tributyl acetylcitrate (ATBC)
15	terephthalic acid (90) isophthalic acid (10)	ethylene glycol	tributyl citrate (TBC)
16	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol (30)	epoxidized soybean oil (ESBO)
17	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol (30)	trioctyl trimellitate (TOTM)
18	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol (30)	dioctyl tetrahydrophtalate (DOTP)

Table 1 (part 3)

		Polyester		Plasticizer
		dicarboxylic acid	diol	
		[the numbers in ( ) are in mole %]		
Practical example	19	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol(30)	poly(ethylene glycol) (PEG)
	20	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol(30)	bisphenol A-ethylene oxide adduct (New Ball-100 *4)
Compara-tive example	1	terephthalic acid	ethylene glycol (70) 1,4-cyclohexanedimethanol(30)	-
	2	terephthalic acid (90) isophthalic acid (10)	ethylene glycol	-

Note) *4 is available from Sanyo Kasei Kogyo Co., Ltd.

Table 2 (part 1)

		Heat shrinking rate (% in transverse direction)					
Practical example		60°C	70°C	80°C	90°C	100°C	110°C
	1	5	38	52	60	67	70
	2	3	23	46	58	60	60
	3	0	18	45	52	50	50
	4	3	40	51	58	63	65
	5	4	43	56	64	68	69

Table 2 (part 2)

	Heat shrinking rate (% in transverse direction)						
		60°C	70°C	80°C	90°C	100°C	110°C
Practical example	6	0	23	43	56	53	54
	9	6	40	62	64	62	62
	8	2	24	62	64	53	63
	9	0	15	48	56	59	50
	10	5	41	64	65	65	65
	11	0	17	56	64	64	65
	12	5	45	66	66	65	68
	13	3	38	60	65	64	65
	14	8	46	56	59	64	67
	15	4	38	58	67	65	67
	16	0	16	57	60	59	59
	17	2	21	63	66	66	66
	18	6	42	65	65	66	66
	19	0	10	58	60	60	59
	20	0	30	65	65	66	68
Comparative example	1	0	2	63	65	68	68
	2	0	3	40	39	38	36

As can be seen from Table 2, the heat-shrinking polyester film of this invention can start to shrink at a relatively low temperature around 70°C which is almost the same as that of the heat-shrinking poly(vinyl chloride) film. Moreover, it is very important that, as the temperature increases, the shrinking ratio increases gradually, which solves the problem of uneven shrinking.

However, in Comparative Examples 1 - 2, which do not contain any plasticizers, the heat-shrinking polyester films show a sudden increase of the shrinking ratio at around 80°C.

Effects of the invention

This invention provides a heat-shrinking polyester film which has excellent low-temperature shrinking properties as well as uniform shrinking capability.

The heat-shrinking polyester film of this invention has good heat resistance and will not generate hydrogen chloride when incinerated as the heat-shrinking poly(vinyl chloride) film does. In addition, since the shrinking ratio increases gradually as the temperature increases, uniform shrinking can be obtained without having any distortions. Therefore, the heat-shrinking polyester film of this invention is very suitable for the shrink labels for various kinds of containers, such as PET container, etc.

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